MOLECULAR-BEAM SAMPLING/MASS SPECTROMETRIC STUDIES OF THE PRIMARY PYROLYSIS MECHANISMS OF BIOMASS, FOSSIL ORGANIC MATTER, AND SYNTHETIC POLYMERS

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INTRODUCTION

A major emphasis in the thermochemical conversion of biomass to fuels and chemicals is on the high heat transfer processes generally called fast pyrolysis (1). The object of fast pyrolysis is to produce high-value, low-molecular-weight products while avoiding the formation of char. This concept has been applied to the formation of hydrocarbon gases (1) and to the direct liquefaction of wood (2) as well as to the flash pyrolysis of coal (3).

One problem in these processes is that the rate and reaction conditions make it difficult to study the sequential reactions that occur, particularly the initial devolatilization or primary pyrolysis steps. This initial product slate is difficult to determine due to the reactivity, thermal lability, and molecular weight range of the products as well as the subsequent condensation or cracking reactions that mask the initial composition.

To accomplish the determination of primary product composition, the flash pyrolysis of samples in 900°C steam/He has been coupled with a molecular-beam sampling system for a mass spectrometer that permits real-time sampling and rapid quenching from ambient hot environments, while preserving reactive and condensible species. This system has been extensively described in two recent publications (4, 5) and is briefly reviewed in the experimental section below.

The major emphasis of this report is on the determination of the primary pyrolysis mechanisms of the fast pyrolysis of lignocellulosic biomass and its major constituents: cellulose, hemicellulose (particularly the pentoses, xylan and arabinan), and lignin. Other carbonaceous materials are also included for the purposes of comparison and demonstrating the technique, but pyrolysis mechanisms will not be discussed. These materials include Texas lignite, Pittsburgh #8 coal, Utah tar sand, Colorado oil shale, high-moor and low-moor peat, polyethylene, and polystyrene. The plastics are included because they are an important component of municipal solid waste and refuse-derived fuel.

EXPERIMENTAL

The fast pyrolysis/molecular-beam sampling/mass spectrometer (Fig. 1) used in this study is run by suspending a quartz boat of material (25-50 mg) in the unignited flame gases (H_2, O_2, and He) and positioned at 5 mm below the sampling orifice. At this position, residence time (5-25 ms) is insufficient for secondary cracking to occur. The flame is ignited and the 900°C steam and helium, which are maintained free of oxygen, heat the sample to pyrolysis and sweep the products away so only promptly-formed gases are introduced into the sampling orifice. Since the initial pyrolysis process is endothermic and essentially ablative, the actual process temperature is well below the 900°C steam/He (1). The sonic sampling orifice rapidly quenches the sampled gases which are subsequently collimated as a molecular beam for introduction into the ion source of a quadrupole mass spectrometer. Low energy electron impact ionization (15.5 eV) is used to minimize fragmentation. The

free-jet expansion of the sampled gases results in rapid quenching and presents internally cooled molecules to the ion source which also minimizes ionization fragmentation.

The two major disadvantages of the technique are: (1) difficulty in quantitation due to mass discrimination in the molecular beam, and variation in ionization sensitivities at low electron energy; and (2) the ambiguity in structure assignment based on only the ion mass.

RESULTS AND DISCUSSION

Biomass

Cellulose pyrolysis has been extensively investigated (6). In Fig. 3 (top) is shown the pyrolysis-mass spectrum (py-ms) of cellulose from 45 to 445 amu. Levoglucosan (Fig. 2, I) is well known to be the major primary pyrolysis product from cellulose in the high temperature pyrolysis regime (7), yet the parent ion (mass 162) is of secondary importance in the spectrum. Work with chemical ionization (8) has shown that under typical ion source conditions, levoglucosan is highly fragmented by EI. The major portion of masses 144, 73, 60, and significant portions of 98 and 126, are due to EI fragmentation of levoglucosan, so caution is required in interpreting py-ms. Nevertheless, from studying model compounds to determine the extent of EI fragmentation, a great deal of insight can be gained from this experimental system. The striking simplicity of cellulose pyrolysis, particularly in the higher mass region, is an indication of the dominance of the transglycosylation mechanism which leads to levoglucosan formation (7). The set of peaks at higher molecular weights (288, 306, 324, 325) is due to dimer formation and is analogous to the 126, 144, 162, 163 series for levoglucosan. The dimer (mass 324) could be due to a glucose-levoglucosan disaccharide, but that substance would probably be of limited thermal stability. Another possibility is the formation of 1',6:4',2-dianhydro-diglucopyranose (Fig. 2, II) by transglycosylation from the hydroxymethyl group of ring 1 to the C-1 of ring 2. Groups analogous to this dimer series have been observed up to mass 1135 (7 units). The odd masses such as 163 and 325 are thought to be EI fragments of higher polymers because the ratios 162/163 and 324/325 decrease as the EI voltage is increased from 15 to 50 eV. These observations are speculative and require collaboration with other experimental systems.

The addition of catalytic amounts of alkali salts has been known to inhibit levoglucosan formation (7). The py-ms of cellulose treated with 5% (mole) K^+ (K_2CO_3) is shown in the bottom of Fig. 3. The simplicity of cellulose pyrolysis has been replaced by a much more complicated spectrum with the noticeable absence of levoglucosan and the dimer. The masses associated with furan compounds are now predominant: 98, furfuryl alcohol; 110, 5-methyl-furfural; and 126, 5-(hydroxymethyl)-furfural. Only 110 is increased in absolute terms above what is obtained in untreated cellulose pyrolysis. Within the low-molecular-weight range, which is not shown here, masses 32 and 43 increase in yield due to methanol and carbonyl compounds, respectively. This treatment also increases the yield of char by a factor of 100. A possible explanation for these observations is that the alkali salt catalyzes the cross-linking between cellulose chains and prevents the steric rearrangements necessary for transglycosylation. This allows the simple fission reactions that yield carbonyl compounds, furans, and methanol to predominate as well as preserving more of the carbon as char.

The hemicelluloses are heterogeneous polysaccharides. Examples are xylans (hardwoods), glucomannans (softwoods), and arabinogalactanes (also classified as an extractive) (9). Only xylan and arabinose will be discussed here since the other hexopyranoses have similar pyrolysis products to cellulose. Xylan is a β-1,4 pento-pyranose polymer that differs from cellulose mostly by the missing hydroxymethyl group (C-6). In native wood, the xylan has acetyl groups bound to the C-2 position as well as minor amounts of glucuronic acid. In the separation technique these

groups are removed and residual salts from the process may have an effect on the pyrolysis of xylan as seen in cellulose pyrolysis. The spectrum shown in the top of Fig. 4 demonstrates that in the absence of the hydroxymethyl group, no simple high-molecular-weight pattern is present. In fact, the spectrum is similar to the one for the alkali-treated cellulose in Fig. 3. The lower-molecular-weight peaks are probably carbonyl compounds (e.g., butanedione, 86) and furan compounds (e.g., furfural, 96). Schulten and Gortz (10) proposed three basic chemical reaction mechanisms to explain the formation of the smaller pyrolysis products: dehydration, retroaldolization, and decarbonylation, but they are probably only important as primary reactions when transglycosylation is prevented, as for xylan, and are more important as secondary cracking pathways. The large peak at 114 has been identified from xylan pyrolysis as 3-hydroxy-2-penteno-1,5-lactone by Ohnishi et al. (11). This is the most characteristic peak of pentoses and is present in both xylan and arabinose although they have pyranose and furanose structures, respectively.

Arabinose is only a minor component of hemicellulose [3.5% of all sugars in softwoods and minor amounts in hardwoods (9)] and is present as copolymers with other sugars such as galactose or xylanose. However, it is discussed here because it clearly demonstrates some of the pathways discussed previously. Arabinose is a pentofuranose with a hydroxymethyl group that undergoes similar transglycosylation reactions as occurs in cellulose pyrolysis. The spectrum in the bottom of Fig. 4 shows a series of peaks, 132, 114, 96 which are analogous to 162, 144, 126 in cellulose. The 132 peak may be due to 1,5 anhydroarabinofuranose which could lose H_2O to form a double bond between C-2 and C-3 and give the peak at mass 114. Alternatively, the 114 peak may be due to 3-hydroxy-2-penteno-1,5-lactone as is proposed by Oshnishi et al. in xylan pyrolysis (11). A dimer peak is present in arabinose (mass 264) in contrast to xylan.

The third major category of biomass constituents is the lignin fraction. The py-ms of two types of separated lignin fractions derived from Aspen wood is shown in Fig. 5. In both cases, the distribution of lignin peaks is different from that observed in native aspen pyrolysis where the lignin hardwood monomers, coniferyl alcohol (180) (Fig. 2, III) and sinapyl alcohol (210) (Fig. 2, IV), clearly predominate. Of the various methods of separating lignin from wood, ball-milling followed by solvent extraction is the least destructive (Fig. 5, top). The steam explosion process (Fig. 5, bottom) changes the distribution of products giving decreased yields of the monomers and increased yields of the smaller fragments. The guaiacol (124) (Fig. 2, VI) series is derived from coniferyl alcohol (180) and includes guaiacol (124), methyl guaiacol (138), ethyl guaiacol (152), and coniferylaldehyde (178). The syringol (154) (Fig. 2, VII) series is derived from sinapyl alcohol (210) and includes methyl syringol (168), ethyl syringyl (182), vinyl syringol (180), propenyl syringol (194), 1-hydroxy-3,5-dimethoxy-benzaldehyde (182), and syringylaldehyde (208). In addition, the steam-explosion process leads to a higher abundance of the higher-molecular-weight dimer peaks (272, 280, 302, 332) which have also been found by high performance size exclusion chromatography of these materials. They probably correspond to β-0-4 alkyl aryl ether structures (Fig. 2, IX) or phenyl coumarin-derived compounds (Fig 2, X) with partially cleaved side chains (12).

Studies of the rate of product formation have shown that not only are the monomer units formed in initially high yields, but they are also the first products to form with smaller lignin fragments such as guaiacol formed later. The evolution of mass 272 reaches a maximum after the monomers, but before the lighter fragments reach maximum evolution. These results suggest that during pyrolysis further cleavage of the higher-molecular-weight polymers into the stable ether dimers occurs. This differential evolution of primary products from lignin pyrolysis is in contrast to cellulose where all products reach a maximum at the same time.

The predominance of the lignin monomers and the peak at mass 272 indicates that an alternative mechanism of formation is likely other than just random bond cleavage.

The β to α carbon-carbon bond of the propyl side chain can be cleaved under pyrolysis conditions. Ether cleavages could also occur.

Some representative biomass samples are shown in Fig. 6. No hardwood sample is shown since the whole aspen wood spectrum closely resembles the ball-milled aspen lignin spectrum in Fig. 5 with the additional contribution from the carbohydrates and the difference in proportions of lignin peaks, with 180 and 210 being the predominant lignin peaks in the whole wood pyrolysis spectrum. The pyrolysis of pine (Fig. 6, top) is typical of softwoods with the large yield of coniferyl alcohol and the presence of the group of peaks at higher molecular weight. The structures of these products are probably derived from the dimer of coniferyl alcohol with a minor peak at 342 due to the condensation of two monomers (360-18). The other peaks in this group are probably due to rearrangement reactions. Of particular interest is the peak at mass 272 since it forms earlier than the other high-molecular-weight lignin peaks and is present in higher abundances. A possible assignment is an enol ether such as (IX). This peak is present in all lignins investigated--kraft, milled wood, organosolv, and steam explosion.

The rice hull pyrolysis spectrum shown in the bottom of Fig. 6 is typical of grasses, which have an additional lignin monomer, p-coumaryl alcohol (mass 150) that is quite often the major lignin monomer peak for grasses. The peak at mass 120 is also common to most grasses and probably is due to the coumaryl alcohol fragment, p-vinyl-phenol. Mass 120 is unusual since it has the same early evolution path as the monomers 150, 180, and 210, unlike other lighter fragments, i.e., guaiacol, that reach maximum evolution significantly later than the monomers. The pentoses also make a significant contribution to the pyrolysis products of grasses judging by the increased yield of mass 114 which is charactertistic of xylan and arabinose (Fig. 4).

PRIMARY PYROLYSIS OF OTHER CARBONACEOUS MATERIAL

The more complex spectra of the pyrolysis products of several other carbonaceous materials are shown in Figs. 7-10 for comparison and are briefly described below. The spectra of two coal samples are shown in Fig. 7a. The pyrolysis products are more difficult to rationalize than the lignin peaks in wood. To facilitate discussion, homologous series of peaks are connected by lines in the figures as is used by Meuzelaar et al. (13).

The less mature Texas lignite shown in Fig. 7 is dominated by the phenolic series (94, 108, 122). Other typical lignin peaks (110, 124, 138, 150, 164) are greatly diminished in this lignite sample. Several naphthalene-derived series are present: tetralin (Fig. 2, XI) (132, 146, 160, 174, etc), dihydronaphthalene (144, 158, 172, 186), and alkyl naphthalene (142, 156, 170, 184), as well as tetrahydroanthracene (182, 196, 210, 224).

The bituminous coal sample, Pittsburgh #8, exhibits different patterns. The phenolic series is decreased in importance (as would be expected for the more mature sample) but the 110, 124, 138 series is enhanced. In addition to the lignin derived methoxyphenols this series could also be due to alkyl dihydroxybenzenes or dialkenes. The dihydronaphthalene series (144, 158, 172, 186) is much more predominant than in lignite and the tetralin and alkyl naphthalenes are not obviously present. The series, 184, 198, 212, 226, 240, which is the same sequence as alkyl naphthalenes, is in this case probably due to hexahydroanthracene, because of the higher-molecular-weight range. The last series outlined (234, 248, 262) may be due to a 4-ring naphthenoaromatic structure with the methyl derivative (248) being the predominant species. This is also the case in the hexahydroanthracene series, and the hydroxy and dihydroxybenzene series, but the dihydronaphthalene series peaks at the 2-methyl derivative (158). This predominance of the methyl

derivatives may reflect the thermal dissociation of aliphatic bonds between condensed naphthenoaromatic structures (14).

The pyrolysis of other geopolymers is shown in Fig. 8. Utah tar sands are bitumen-impregnated rocks and not strictly geopolymers, but thermal recovery is a promising method of processing tar sands to recover lighter products (15) and so tar sands are discussed here. The pyrolysis of Utah tar sand is shown in Fig. 8 and although it appears simpler than the spectra for coal, the patterns or homologous series are not as well defined. An alkene series is present (84, 98, 112, 126), but no significant series is present for the saturated hydrocarbons. The series 82, 96, 110, 124 may be due to the dialkene series although some contribution from methoxyphenol is also possible. The high abundance of mass 96 favors the dialkene interpretation since this can not be due to a phenolic or methoxyphenol ring structure.

The Colorado oil shale pyrolysis spectrum is dominated by the lighter materials including alkenes (56, 70, 84, 98), dialkenes (68, 82, 96, 110, 124), trialkenes (80, 94, 108, 122, 136), and tetraalkenes (106, 120, 134, 148, 162). The series 144, 158, 172, 186 may be due to dihydronaphthalene. The series of odd masses (195, 209, 223, etc.) could be due to fragment ions of higher-molecular-weight alkenes, although no dominant parent peaks occur at higher molecular weight.

The pyrolysis spectra of two peat types are shown in Fig. 9. Peat #1 is a high-moor peat, which is derived primarily from mosses (Sphagnum), cotton grass, and heath plants (16). The pyrolysis products are predominately carbohydrate in nature with only a minor contribution from lignin. Despite the predominant masses 144 and 162 which are attributed to levoglucosan, the higher-molecular-weight range does not show the peaks characteristic of the dimer species (see Fig. 3) for cellulose, which may be due to the heterogeneity of the sample compared to pure cellulose.

Peat #2 is a low-moor peat (composed of plants with a higher lignin content). The pyrolysis spectrum reflects the presence of lignin with the methoxyphenol series (124, 138, 152) present. The actual lignin monomers (150, 180, 210) are not as predominant as in fresh biomass materials, which may be due to the effects of diagenesis on lignin structure (17). There is also a distinct lack of prominent high-molecular-weight peaks (such as mass 272) in this sample as well; instead, all even masses are present in rougly equal abundance.

The pyrolysis spectra of two common plastics, polystyrene, and polyethylene, are shown in Fig. 10. Both these polymers show the formation of homologous series of products. The pyrolysis of other polymers yields only the monomer, such as polytetrafluoroethylene and poly(methyl methacrylate), while a third group breaks down into complex arrays of products such as polyvinylchloride and polyamide (nylon). The polystyrene and polyethylene, however, give this same repeating pattern shown in Fig. 10 to molecular weights greater than 1400 amu.

The dominant peaks in the polystyrene spectrum are due to the monomer (104), dimer (208), ad trimer (312). The other masses represent pyrolysis products not seen in other py-ms systems (13). Mass 116 could be due to indene (Fig. 2, XII), which would require cyclization of the aliphatic backbone to form the ring system. The peak at 130 could then be assigned to methylindene. Mass 142 could be assigned to methyl-naphthalene, analogously (with substantial rearrangement of the aliphatic chain).

There are several ion series present in the polyethylene spectrum: alkyl fragment ions (57, 71, 85, 99, 113, . . .), alkenyl fragment ions (55, 69, 83, 97, 111, 125, . . .), alkenes (196, 210, 224, 238, 252, 266, . . .), and dialkenes (194, 208, 222, 236, 250, . . .). These products indicate that random bond cleavage is occurring followed by hydrogen rearrangement to yield a saturated end and an unsaturated end (the alkenes), although there is a high proportion of molecules having two unsaturated ends (the dialkenes). The extent of condensation reactions is unknown.

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CONCLUSIONS

Biomass samples give a relatively simpler spectrum of products compared to the product slate obtained from organic geochemical samples. In the latter materials, a higher degree of sample heterogeneity, diagenesis, and humification may explain most of the differences.

Cellulose pyrolysis at high temperature is dominated by levoglucosan possibly as a result of transglycosylation reactions, which depend on the hydroxy methyl group for sterically favored attack. Higher anhydro-polymers may also be formed by inter-ring attack by the primary hydroxyl group. A competing mechanism is evident in the presence of alkali metal salts: bond fission reactions which yield carbonyl compounds, furans, and methanol.

Lignin, although of a more complicated structure, also yields relatively simple primary pyrolysis products dominated by the three precursor monomers that make up the macromolecule, although the contribution from smaller fission products is more significant than in the homogeneous polymer, cellulose. The formation of higher-molecular-weight products from lignin also indicates the predominance of specific rearrangemnt reactions over simple bond fission. An example is the predominance of the peak at mass 272 in all the lignin samples investigated, irrespective of genetic origin or method of preparation.

The complexity of the pyrolysis spectra of coal, tar sands, oil shale, and to a lesser extent, peat indicates the greater importance of labile bond fission in the pyrolysis of geopolymers.

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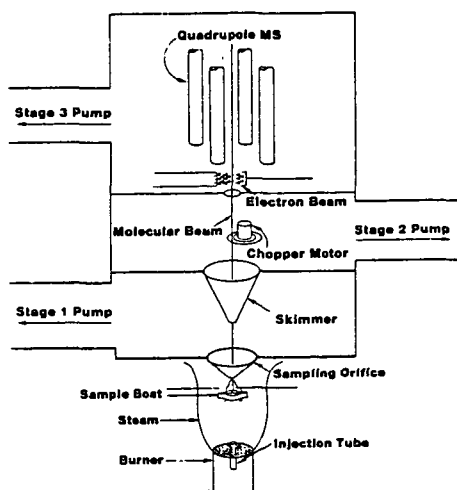
Figure 1.   Molecular-Beam Apparatus for Fast Biomass Pyrolysis.

III: R1 = OME, R2 = H
      R3 = CH=CH-CH2OH

IV: R1 = OME, R2 = OME
      R3 = CH=CH-CH2OH

V: R1 = H,   R2 = H
      R3 = CH=CH-CH2OH

VI: R1 = OME, R2 = H
      R3 = H

VII: R1 = OME, R2 = OME
      R3 = H

VIII: R1 = OME, R2 = H
      R3 = CH=CH-CH3
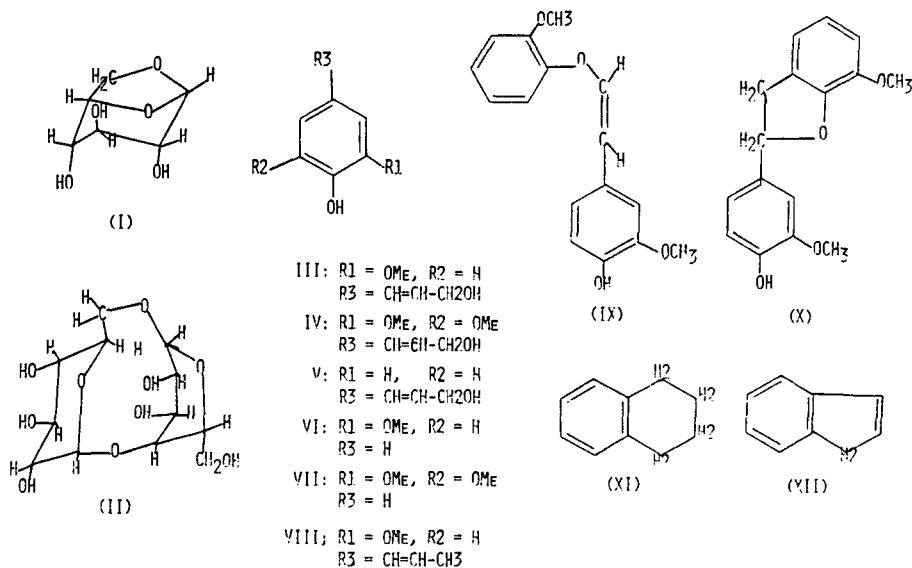
Figure 2.   Selected Structures Referred to in Text.

CELLULOSE

XYLAN

ARABINOSE

CELLULOSE + 5% K(K2CO3)
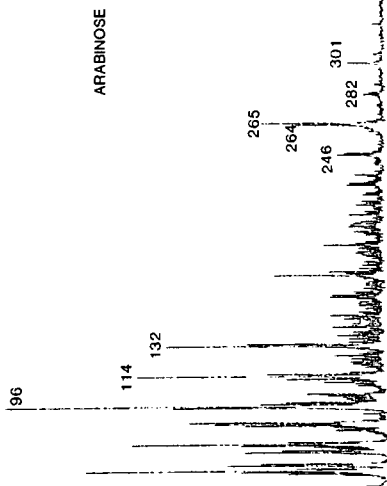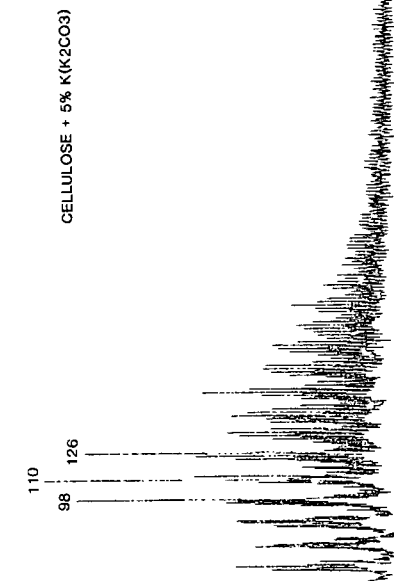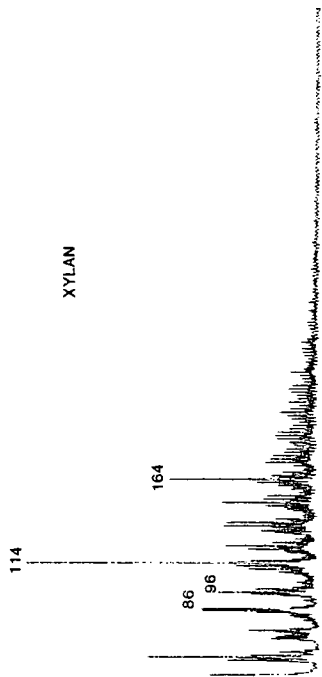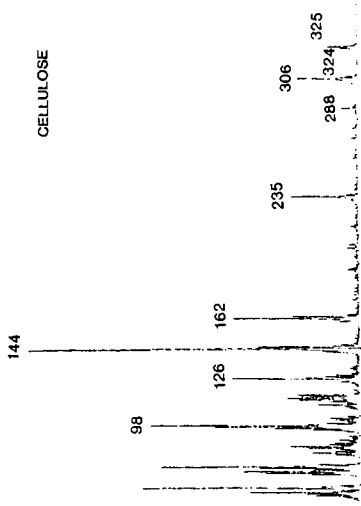
Figure 3. Mass Spectra of Primary Pyrolysis Products From Cellulose (Top) and Alkali Treated Cellulose (Bottom).

Figure 4. Mass Spectra of Primary Pyrolysis Products From Xylan (Top) and Alkali Treated Aribinose (Bottom).

BALL-MILLED ASPEN LIGNIN

79 124 138 154 168 180 194 210 234 272
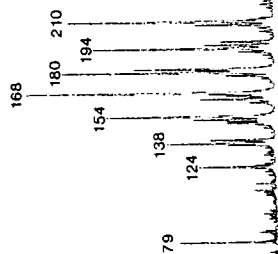
MEOH EXTRACTED
STEAM-EXPLODED
ASPEN LIGNIN

194

96 110 124 138 154 168 182 210 272 280 302 332

PINE

180

57 73 85 98 114 126 138 144 150 164 204 226 272 264 298 312

RICEHULL

85 98 114 120 126 138 150 164 180 194 272
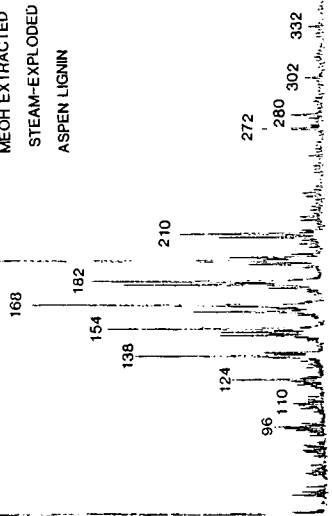
Figure 5. Mass Spectra of Primary Pyrolysis Products From Ball-Milled Aspen Lignin (Top) and Steam-Exploded Aspen Lignin (Bottom).
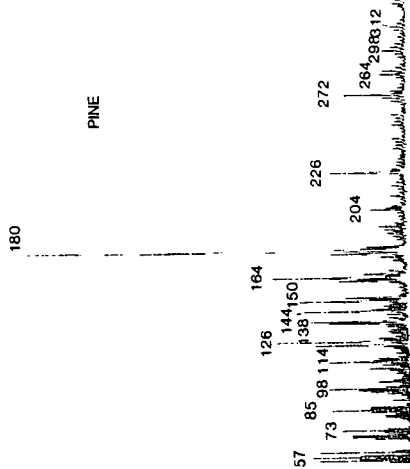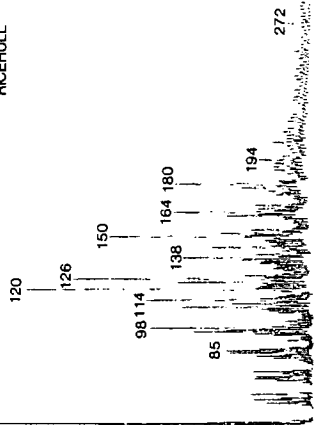
Figure 6. Mass Spectra of Primary Pyrolysis Products From Pine (Top) and Rice Hulls (Bottom).

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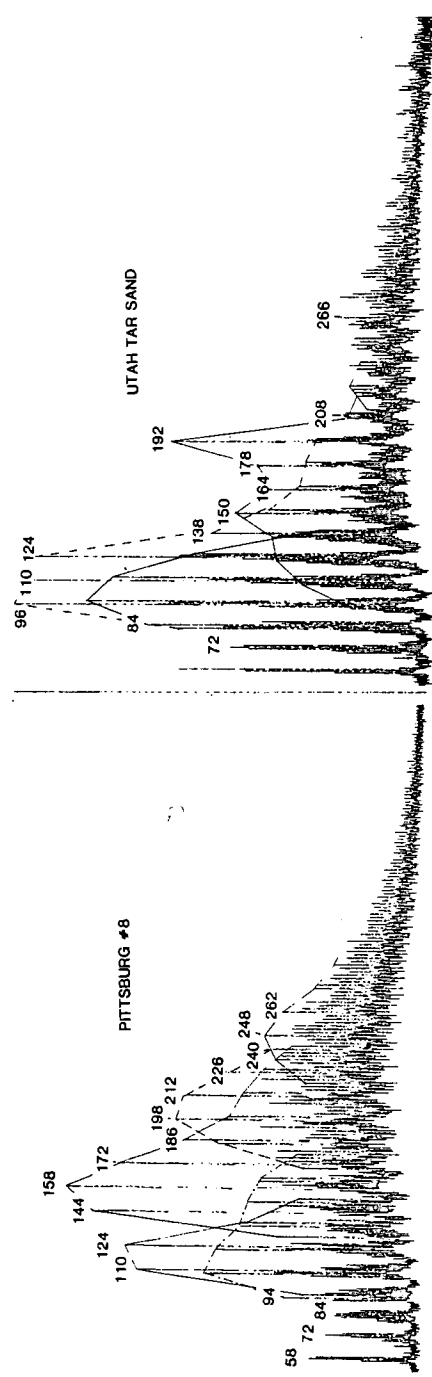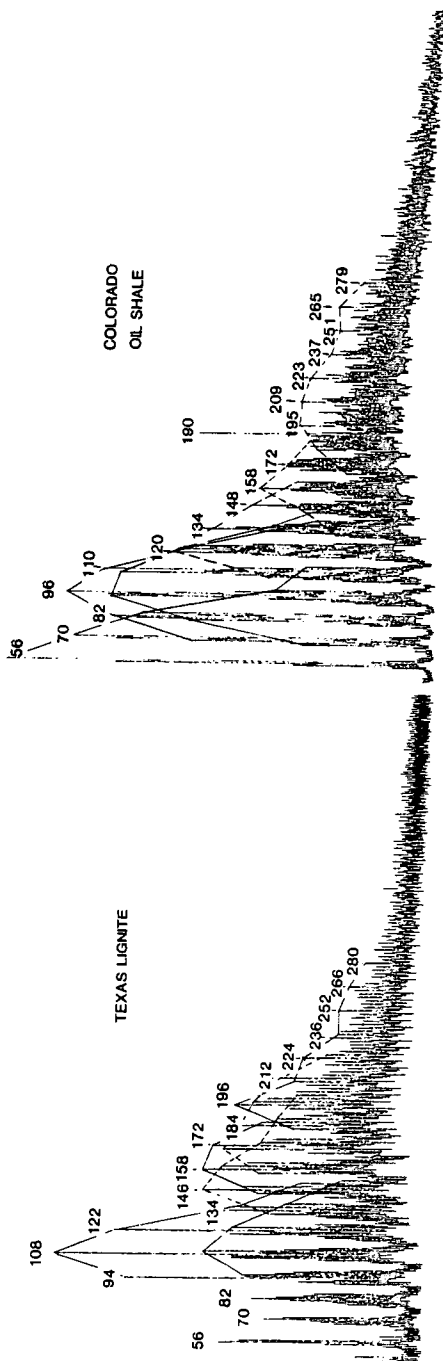
Figure 7. Mass Spectra of Primary Pyrolysis Products From Texas Lignite (Top) and Pittsburgh #8 Bituminous Coal (Bottom).

Figure 8. Mass Spectra of Primary Pyrolysis Products From Colorado Oil Shale (Top) and Utah Tar Sand (Bottom).
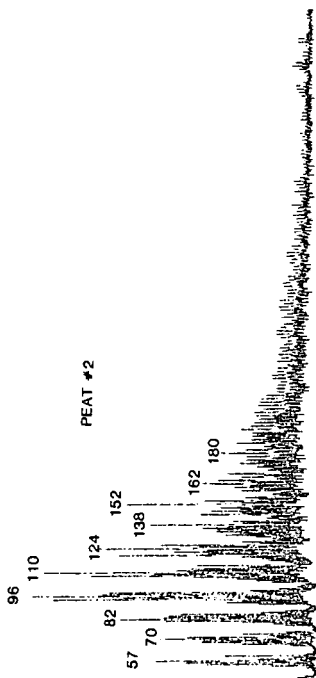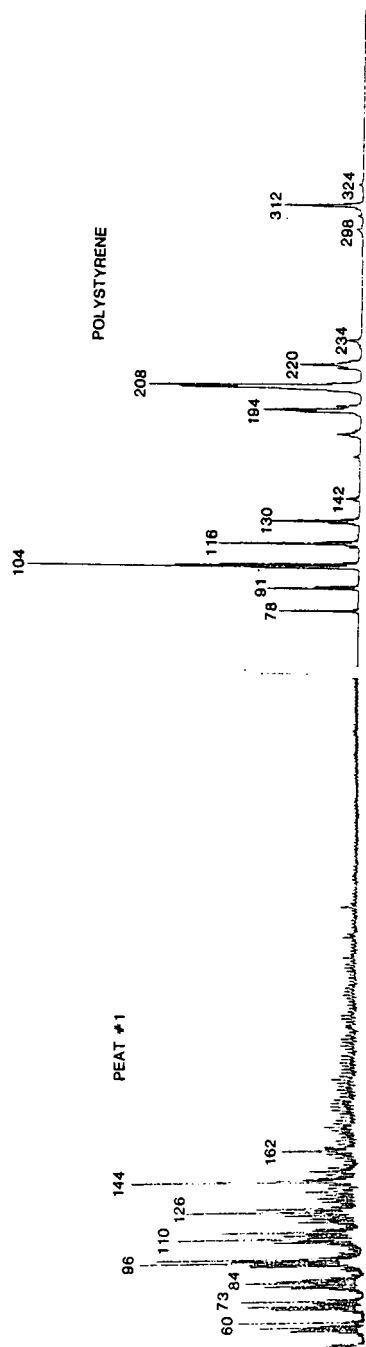
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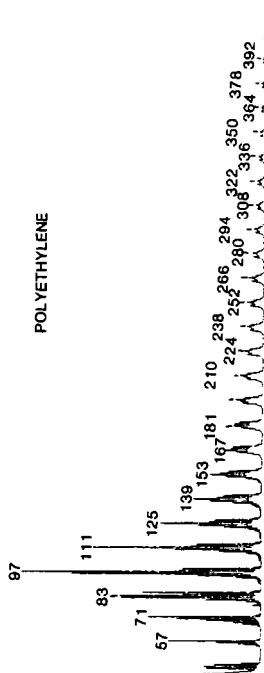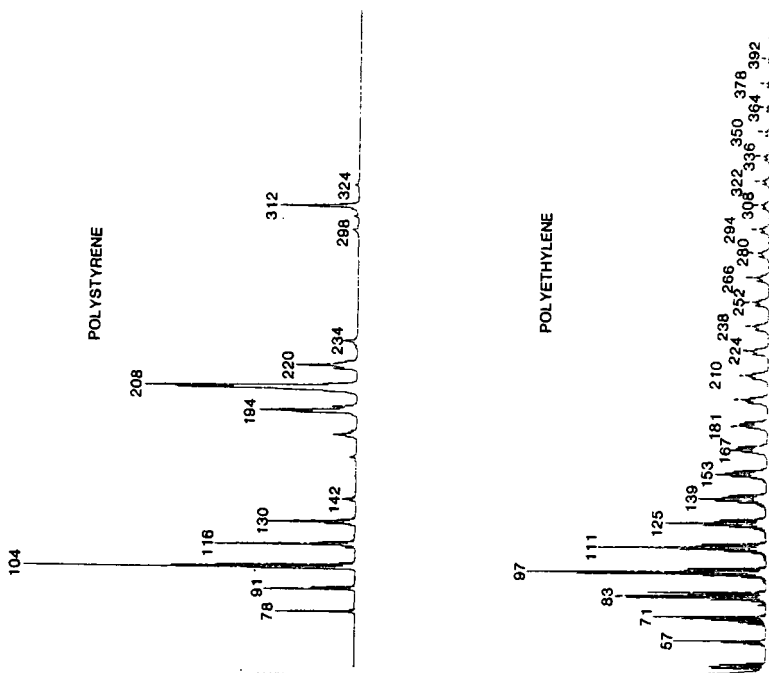Figure 9. Mass Spectra of Primary Pyrolysis Products from High-Moor Peat (Top) and Low-Moor Peat (Bottom).

Figure 10. Mass Spectra of Primary Pyrolysis Products From Polystyrene (Top) and Polyethylene (Bottom).

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